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STUDY OF ANODES IN ELECTROLYSIS OF COPPER
LEACHING SOLUTIONS CONTAINING
CHLORIDES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Louis F. Stuebe

ENTITLED Study of Anodes in Electrolysis of

Copper Leaching Solutions Containing Chlorides

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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STUDY OF ANODES IN ELECTROLYSIS OF
COPPER LEACHING SOLUTIONS CONTAINING CHLORIDES

Part I

Introduction

This work is interested in the study of the corrosive effects of copper leaching solutions containing chlorides upon the anode during electrolysis.

Many copper ores are more economically leached and electrolyzed directly from the leaching solution than by roasting, smelting, and subsequent electrolysis. In fact there is reason to believe that in the future almost all ores that show this advantage will be electrolyzed, thereby eliminating the great outlay in smelting plant and the great cost of fuel. Moreover the whole process will be entirely under the control of the mine operator, who will not have to ship his matte to the refineries and depend upon them for the speed of his turnover.

The requirements of a plant for the electrolysis of copper leachings would be a choice of the various leaching processes of which there are now several rather highly developed, and a dependable source of electrical current which is easily obtained in our mountains from hydro-electric stations. The other requirement, which is the primary one and has thus far probably been the chief cause for the reluctance of operators to establish it, is the electrolysis process itself; which means the study of the character of the leaching solution, the control of the

current, and the type of anode.

This problem is primarily concerned with the study of the anode when the analysis shows the presence of chlorides.

In this thesis the work has been carried to the study of iron alloy oxides only as the author was unexpectedly halted in his work. However as the preliminary study has covered the field of all types of anodes in general and their probable development to obtain the desired non-corrosive anode for copper chloride solutions, and to assist any who may continue this study, he has included in the history and conclusion such information as he has considered of value in the continuation of this study.

Part II

History

The corrosion of all anodes in copper electrolysis is known to be an unavoidable loss. To be sure the ideal anode would be an absolutely non-corrosive one. However among anodes there is a big difference in the degree of solubility of the same in their electrolytes. Consequently when an anode shows little corrosion, as lead in copper sulphate solution, it is termed as non-corrosive. Again an anode may be non-corrosive in one electrolyte and be quite corrosive in an electrolyte of slightly different composition. In addition the efficiency of the process depends upon the character and temperature of the electrolyte, the current density, and the voltage; all of which must be considered along with cost of anodes in determining the economical value of a given process.

These are the conditions which contribute to the complications involved in the study of anodes in electrolysis of copper leachings.

- The industrial electrolysis of copper leaching solutions is in general this:

The copper ore composed of chalcocite, azurite, malachite, along with other minerals, is first crushed fine in rolls and roasted as in the Laszczyński process. Then it is leached with dilute sulphuric acid, or with dilute sulphuric acid and ferric sulphate solution as in the Siemens-Halske process.² Consequently the leachings contain copper sulphate, ferrous sulphate, ferric sulphate, acid,

and other impurities.

The copper leachings are then introduced into wooden vats, many of which are lined with pitch or asphalt. These vats vary in design and capacity, but an average may be taken as $4\frac{1}{2}$ feet deep, $3\frac{1}{2}$ feet wide, and 6 feet long. The leachings are run in by a circulation method, that is, the solution runs from vat to vat by gravity, varying in concentration, or it is electrolyzed in one vat until depleted of copper. After this the liquor is sent back to act as new leaching solution. Generally in either case some means of maintaining circulation is employed. This is occasionally done mechanically, by flow of electrolyte, or by bubbling gas through the solution as is done in the Carmichael process, in which SO_2 is passed through not only for stirring but also to furnish fresh sulphuric acid and assist at depolarization.

The cathodes are copper sheets about $1/32$ inch thick and $3\frac{1}{2}$ by 3 feet with a heavy cross-bar across the top as contact arms. They are generally given a thin coat of glue or engine oil before being started in order to give a uniform and well adhering plate.

The anodes are of various material and measure the same as the cathodes except that they have varying thicknesses. They also have a strong contact bar across the top.

Along the upper edge of each of the two long sides the vats have heavy copper bus-bars to make contact with the cross contact bars of the cathode and anode. One

is positive and the other negative, and are so arranged that the positive makes contact with the anode, and the negative with the cathode.

The ordinary voltage for simple sulphate leaching solution is 2.25 to 2.50 volts, and the current density is 18 to 20 amperes per square foot of cathode surface.⁴

The corrosion of anodes in general is quite well understood in the electrolysis of copper sulphate solutions as used in the Laszczyński or Sieman-Halske processes. In fact the process is very simple when no iron is present, in which case lead anodes are used to the greatest advantage.

However in the presence of iron sulphate some handicaps arises from the polarization of the ferrous and ferric ions. For best results, control of the ferric sulphate concentration is essential as this impurity reduces current efficiency, causes poorer deposition of copper, and when the copper concentration becomes low in the presence of iron sulphate, an additional decrease in efficiency is observed.⁶ The lowering of efficiency is due to the solvent action of

ferric sulphate upon the deposited copper.⁷ As the regenerated sulphuric acid or ferric sulphate solution is used over and over again, the ferric sulphate becomes so concentrated that soon all the copper is redissolved. Thus ordinary resolution at the cathode is 2%; but when ferric sulphate reaches the concentration of 25%, it will corrode cathode copper to such an extend that 8 amperes will be required to merely replace.³ The formation of ferric sulphate is prevented by inclosing the anode in porous material to

prevent transference of ferric ions; thus tight fitting bags are frequently used, the thickness of the cloth varying inversely as the strength of the current.⁷

This illustrates the disadvantages of iron in the electrolyte, a metal which is present in all copper leachings. Nevertheless lead anodes are used the same as in simple copper sulphate solution, the lead anode merely peroxidizes and sulphatizes slowly as it is slightly attacked by the free oxygen and the sulphate radicle.³

But when chlorides are present, lead will no longer serve as anode as corrosion is too rapid. Chlorides have a corrosive effect which is little understood electrochemically or otherwise, and as valuable copper leaching solutions are known that contain chlorides in considerable amount which can not be removed to any advantage, it behooves the metallurgist of plants having such leachings to find a non-corrosive anode which is economical enough to put this copper on a competitive market with copper from copper sulphate leachings.

As an examination of the literature shows that chlorides in copper leaching solutions are considered as merely to be avoided, and no strictly theoretical explanation has been made for the apparent cause why these solutions behave so much different from sulphate solutions, the author has had reference only to such practical work as has been experimentally undertaken from time to time to solve this problem.

The Hoepfner process using leachings containing cuprous chloride has been developed. It uses two compartments, anode and cathode, each containing the leachings, and for an anode uses carbon. The two compartments are separated by a permeable diaphragm. However it has been found unsuccessful on account of the short life of the diaphragm and the corrosion of the carbon anodes.

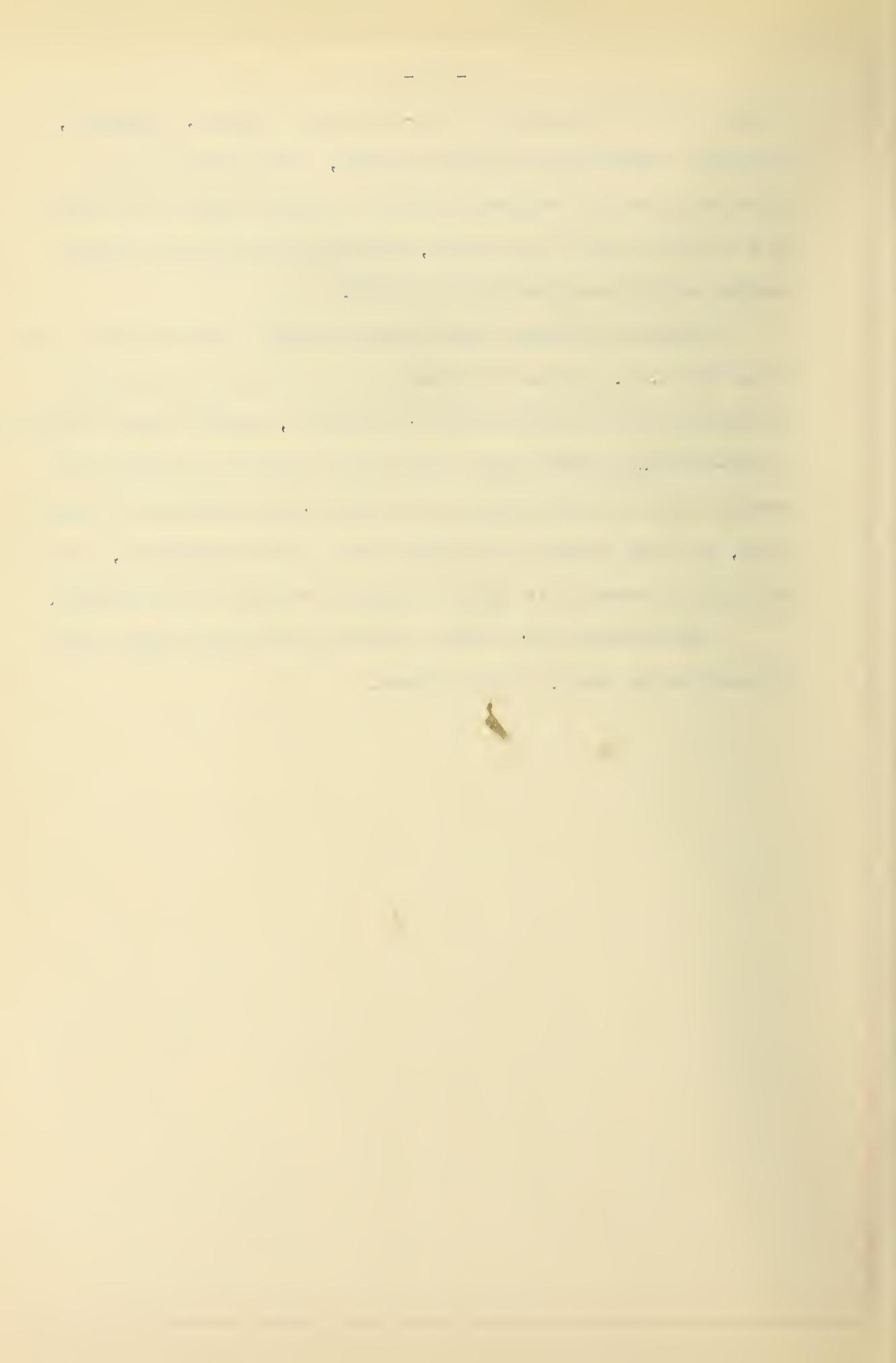
When leaching solutions contain chlorides, fused magnetite or ferro-alloys, generally ferro-silicon, is now used.³ Where an efficient depolarizer is employed, besides the materials mentioned above carbon may be used, however depolarization must be complete.

The Chile Exploration Co. used fused magnetite anodes in their South American plant in a leaching and chlorination process until no more could be purchased from Germany. In their research department at Perth Amboy, N. J. they found the best substitute to be 15% ferro-silicon or "duriron". This is not as good as magnetite, as found by use in their 10,000 ton plant, as it required 15% more energy and raised the temperature too high for the asphalt insulation that was used in the vats.¹¹ Later Colin G. Fink, now director of the Chile Exploration Co., said that 13% ferro-silicon has been found superior to lead and magnetite as an insolvent anode in electrolytes containing not only sulphuric acid, but also nitric. Although no mention is made of chlorides, the statement of being successful in nitric acid may be taken as meaning hydrochloric as well. He goes on to say that next to ferro-silicon, the ferro-chromes are

industrially important as non-corrosive alloys. However, although chemically corrosion proof, they are not very electrolytically corrosion proof. He says that 60% chromium and 40% iron is the best, and in addition that nickel-chrome alloys are becoming popular.

However a recent letter received in the spring of 1922 from the U. S. Bureau of Mines by the Division of Applied Chemistry of the University of Illinois, stated that although ferro-silicon alloys have been found the most satisfactory anodes in the electrolysis of copper ores containing chlorides, yet the results were far from being successful, and said that research in this direction should be encouraged.

Consequently the author started this work under the directions of Asst. Prof. Putnam.



Part III

Experimental

It was decided to investigate the subject of anodes thoroughly and particularly along the line of alloy steels of various compositions.

The study of nickel was first undertaken as several specimens of this alloy of varying composition were on hand. This was to be followed by work on ferro-chromes, and possibly aluminium alloys. Ferro-silicons were only to be considered in special forms as the oxides as it was felt that the pure alloys have been fairly well investigated.

- It developed that time was only available to investigate the nickel alloy to the extend herewith set forth.

All investigation were conducted on the oxidized alloy. The variable factors were these:

Composition of alloy

Method and time of oxidation

Voltages and currents

The solution used was considered representative of such solutions found in the leaching of copper ores containing chlorides. It was this:

Solution #1

3% Cu	(2½% CuSO ₄ • 5H ₂ O	-	100.0 gm.
	(½% CuCl ₂	-	10.6 "
1% Fe	FeSO ₄	-	27.1 "
½% H	HCl	-	13.5 cc.
water		To make one lit	

- The method of applying an oxide coating was this:

Equal parts of sodium and potassium^{nitrate} were placed in an iron crucible, melted and superheated to 500 degrees Centigrade, when black oxide of manganese was added, one part to fifty by volume, and then the superheating continued to 600 degrees Centigrade. The alloy anode was thoroughly cleaned by burnishing and a thin coat of lubricating oil applied. This was then dipped directly in-to the molten bath for a variable period. It was then quenched in cold water and heated in boiling water. Then it was dipped in a hot heavy lubricating oil at about 200 degrees to remove all traces of water. When the anode was to be used, it was boiled in a dilute solution of potassium hydroxide to remove the adhering oil, rinsed in water, and dried. The coating was a jet black oxide.

The first experiments were conducted on 5% nickel-steel as a short preliminary experiment on 3% nickel-steel showed little encouragement. The final experiments were conducted upon 30% nickel-steel.

In each case solution #1 was used, copper foil for cathode, and the distance between anode and cathode was maintained the same in all cases at 2 inches. The current was controled by a resistance reostat in the line, and a carbon block resistance in parallel with the cell. The voltage in all cases was maintained constant, and with this factor constant it will be seen that any variation in amperage in the various runs was due to variation in the

degree of resistance of the anode surfaces. The solution was not circulated or replenished, but was run to a fair exhaustion of the copper. Temperature was room temperature.

Experiment #1

Solution #1 5% Ni-steel, oxidized 3 min.

Voltage maintained at three volts.

Amperage as shown in Tab. I , and figureII,
pp. 12 and 13 respectively.

Exp. #2

Solution #1 5% Ni-steel, oxidized 10 min.

Voltage maintained at 2.5 volts.

Amperage as shown in Tab. I, and fig. I.

Exp. #3

Solution #1 5% Ni-steel, oxidized 10 min.

Voltage maintained at 2.0 volts.

Amperage as shown in Tab. I, and fig. I.

From the tables and graph it is seen that the 10 minute oxidation made it possible to have the same amperage at a lower voltage, 2.5 volts, as compared to 3 volts for the 3 minute oxidation. Also the flatter curve shows it to be more constant and able to maintain itself better.

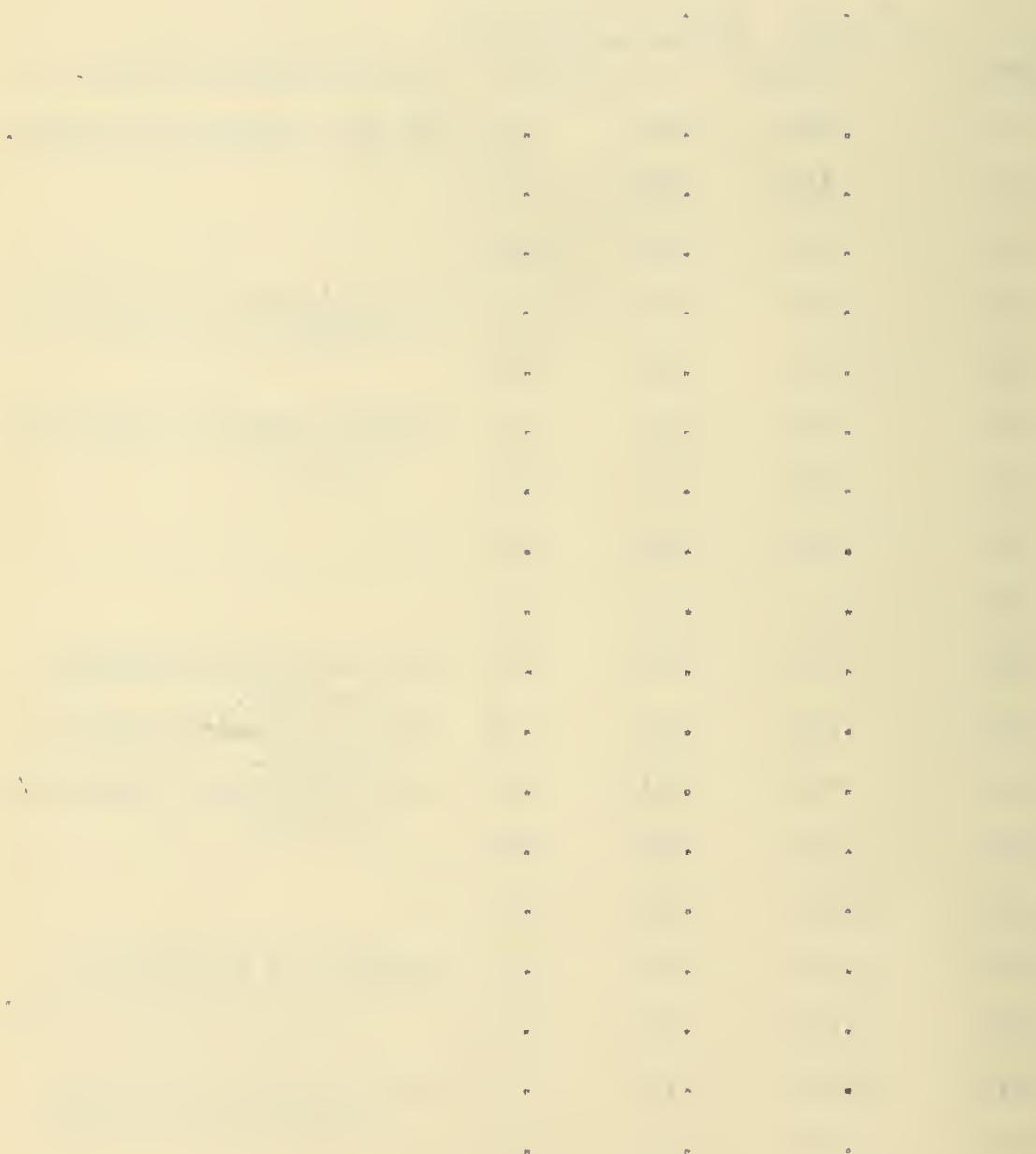
The 10 minute oxide at 2 volts and 2.1 ampere shows the best result on this alloy and its observations are noted in the tables.

Corrosion of the anode in each case was quite uniform and deep beyond the point to classify them as non-corrosive.

One encouragement was the low voltage at which a

Tables I

Time	5% Ni-steel		Solution #1	Constant Voltages
	Exp. #1 3 volts	Exp. #2 $2\frac{1}{2}$ volts	Exp. #3 2 volts	
	Current	in amperes		Observations on Exp. #3
0	.30	.30	.21	No gas evolved at anode.
15	.35	.30	.25	
30	.37	.30	.28	
45	.37	.31	.30	Cu begins to deposit on anode.
60	.39	.33	.32	
75	.43	.37	.36	Scales begin to form on anode.
90	.49	.42	.41	
105	.62	.47	.43	
120	.74	.52	.43	
135	.79	.55	.43	Cu on cathode deposits rapidly.
150	.85	.58	.47	Cu on cathode becoming spongy.
165	.93	.60	.48	Gas beginning to come off cathode.
180	1.00	.63	.48	
195	1.03	.68	.49	
210	1.06	.75	.50	Spongy Cu on cathode forming very rapidly.
225	1.07	.76	.50	
240	1.06	.77	.57	Considerable gas being evolved at cathode.
255	1.05	.77	.. .58	



Amperage-Time Curve
of 5% Nickel Steel oxidized
at Various Voltages (constant)

2 Volts — #3 oxidized 10 min.
2.5 Volts — #2 " 10 "
30 Volts — #1 " 3 "

CURRENT - Amperes

1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

Time Elapsed - Minutes

175

150

125

100

75

50

25

0

250

225

200

175

Figure I

strong flow of current may be maintained, thereby showing an improvement over lead or ferro-silicon, as well as magnetite anodes in efficiency.

Consequently 30% Ni-steel was experimented upon. These specimens were about one-half the size of the 5% Ni-steel, and the oxidation was done thus:

Exp. #	6	7	8	9	10	11	12
Time	8-8	7-7	6-6	5-5	18	15	12

The double numbers indicate that the anode was oxidized for two periods each of the length of time given.

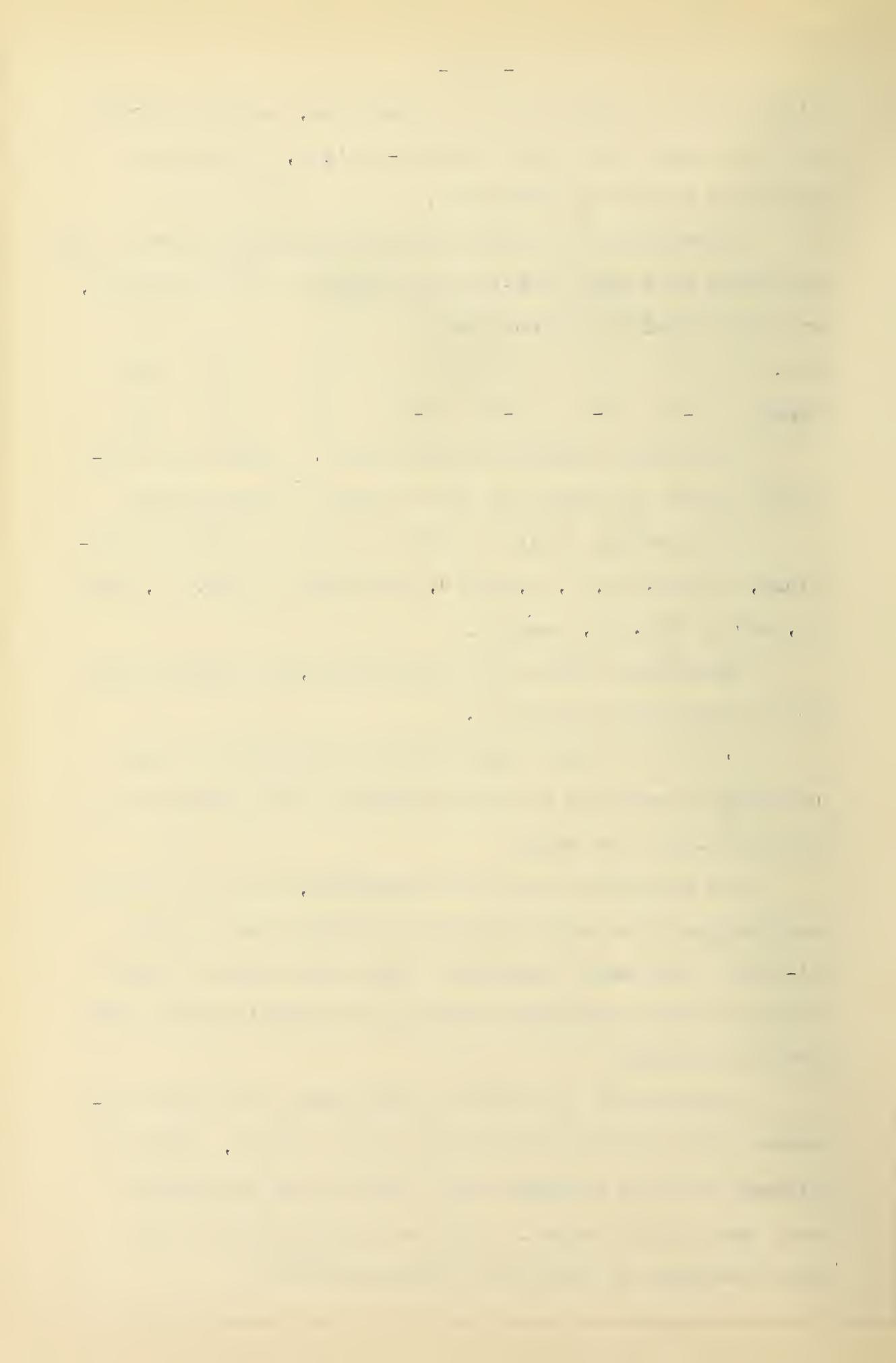
The amperage variations for all of the double oxidations, or Exp. #6, 7, 8, and 9, are given in Tab. II, page 15, and on fig. II, page 17.

Experiment 8 gave the best results, and observations for it are noted in Tab. II.

It will be noted that by double oxidation it was possible to maintain a current density of one ampere for some time with two volts.

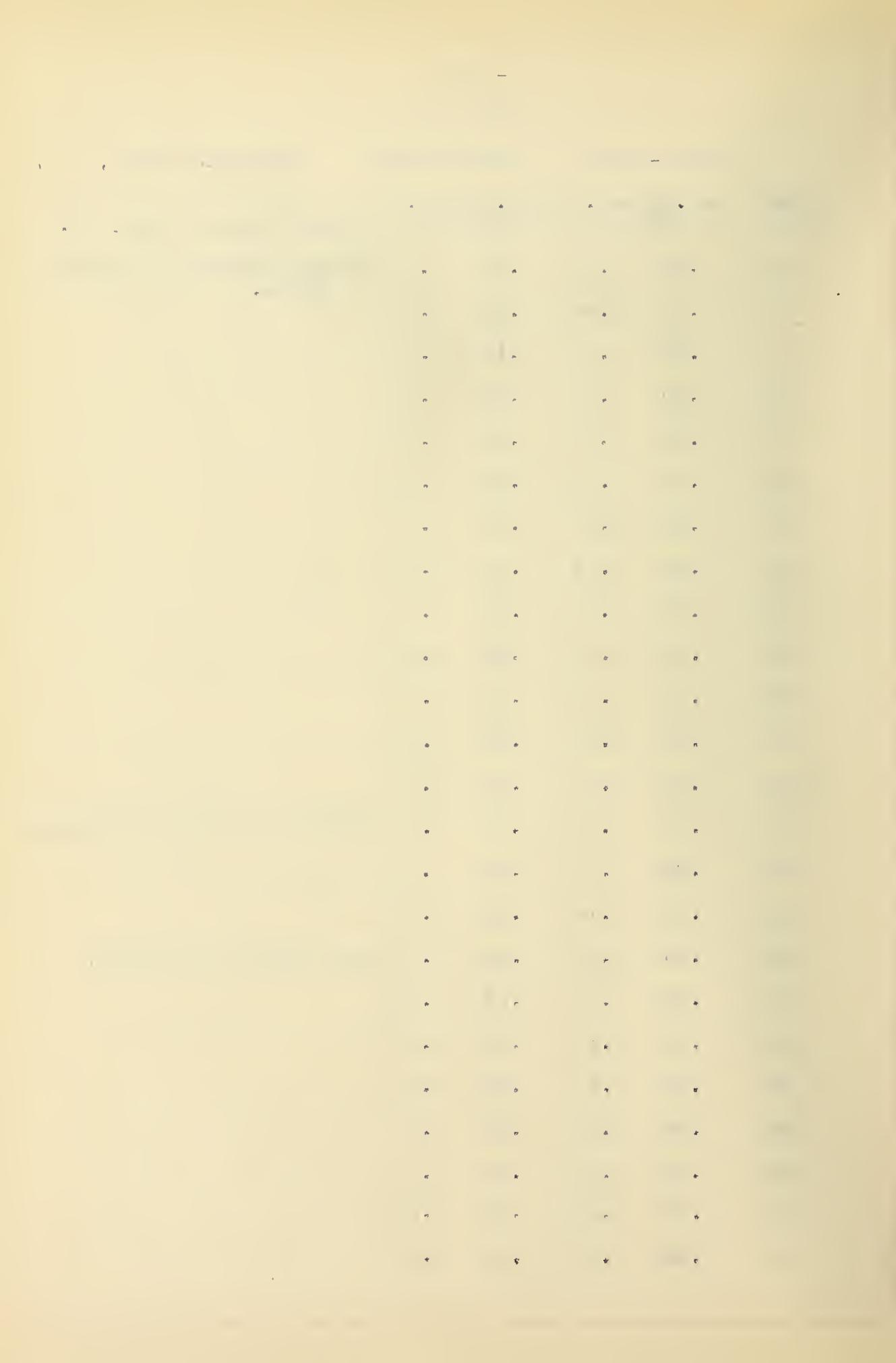
The corrosion was quite pronounced, but for the much smaller area the results were much better than with 5% Ni-steel. The most noteworthy result was that the oxide surface showed pronounced evidence of protecting the lower area in sections.

Incidentally it should be mentioned that it was observed when drilling the holes for the contact, that the highest oxidized specimens were soft on the surface and very hard in the center. This was probably due to the heat treatment of the metal during oxidation.



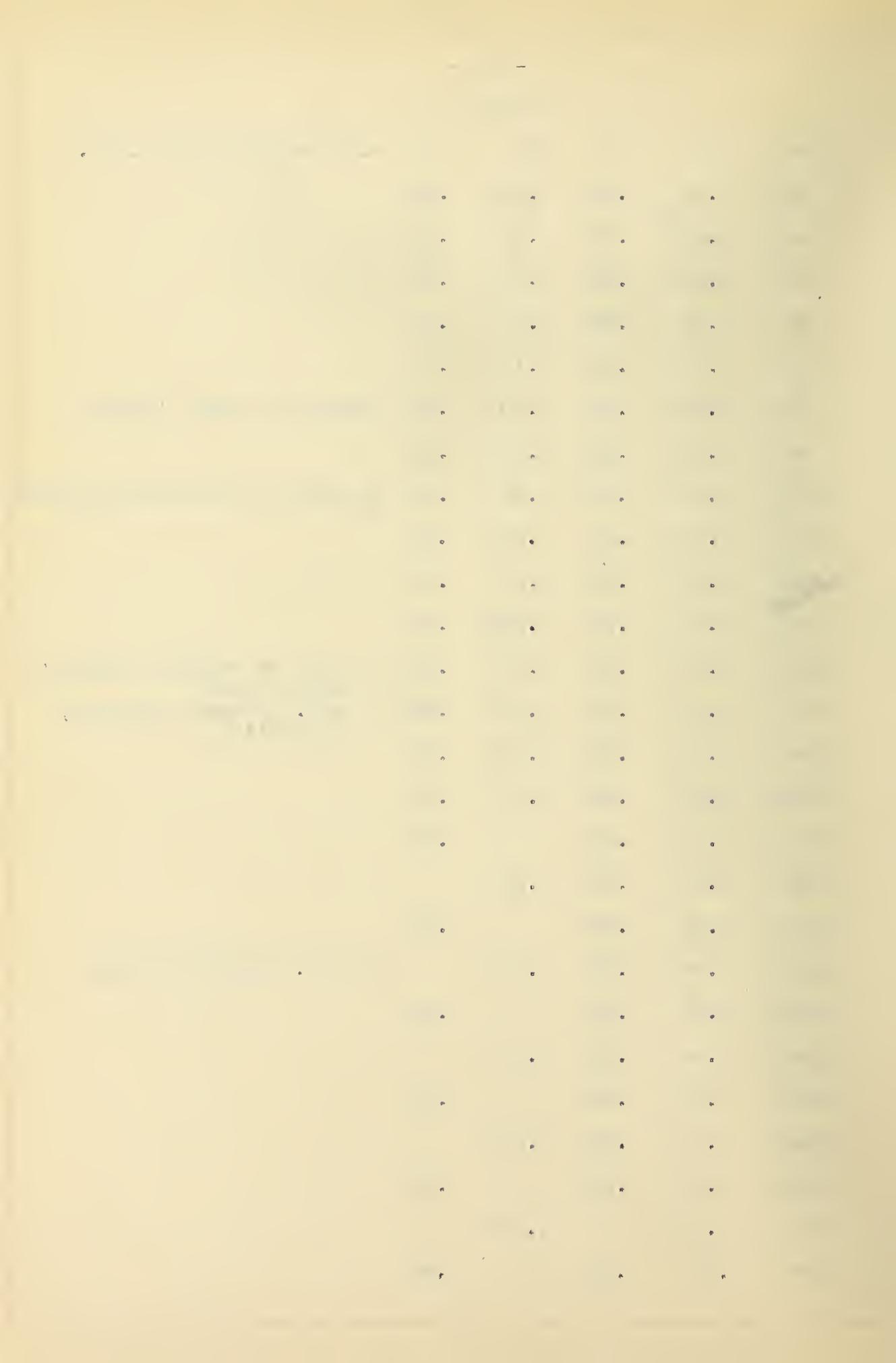
Tables II

Time min.	30% Ni-steel	Solution #1	Constant Volts, 2 v.		
	Exp. #6	Exp. #7	Exp. #8	Exp. #9	
	Current in amperes			Observations on Exp. #8.	
00	.10	.10	.10	.10	Slight evolution of gas at anode.
2	.10	.10	.10	.10	
4	.10	.10	.10	.10	
6	.10	.10	.10	.10	
8	.10	.10	.10	.10	
10	.12	.10	.10	.10	
12	.16	.10	.10	.10	
14	.19	.10	.10	.10	
16	.20	.10	.10	.10	
18	.21	.10	.10	.10	
20	.21	.10	.10	.10	
22	.22	.10	.10	.10	
24	.24	.11	.10	.10	
26	.25	.12	.10	.10	Evolution of gas decreases.
28	.26	.13	.11	.10	
30	.27	.14	.11	.10	
32	.28	.15	.12	.12	Gas evolution stopped.
34	.28	.16	.12	.13	
36	.29	.16	.13	.14	
38	.30	.17	.13	.16	
40	.34	.18	.14	.17	
42	.36	.18	.14	.18	
44	.37	.19	.15	.18	
46	.38	.19	.15	.18	



Tables II

Time	#6	#7	#8	#9	Observations on Exp. #8.
48	.40	.20	.15	.19	
50	.40	.20	.15	.19	
55	.42	.22	.16	.22	
60	.43	.23	.17	.24	
65	.44	.25	.18	.26	
70	.45	.27	.20	.29	Flaking on anode begins.
85	.44	.31	.25	.35	
100	.44	.35	.28	.40	Cu begins to deposit on anode
115	.44	.36	.30	.41	
130	.44	.37	.31	.40	
145	.43	.37	.32	.40	
160	.43	.37	.32	.39	Cu dep. on cathode becoming crystalline.
175	.43	.36	.32	.38	Cu dep. on anode becoming crystalline.
190	.42	.36	.32	.37	
205	.41	.35	.32	.37	
220	.40	.35		.36	
235	.40	.35	.32		
250	.40	.34		.35	
265	.39	.33	.30		Cu dep. becoming spongy.
280	.39	.33		.33	
295	.39	.32	.27		
310	.39	.32		.32	
325	.38	.32	.26		
340	.38	.31		.30	
355	.38		.25		
370	.37	.31		.28	



Amperage - Time Curve
of 30% Nickel-Steel at Two Volts
Oxidized Various Periods

#6
#7
#8
#9

2-8 minutes
2-7 "
2-6 "
2-5 "

.6

.5

.4

.3

.2

.1

Current - Amperes

0 40 80 120 160 200 240 280 320 360 400

Time Elapsed - Minutes

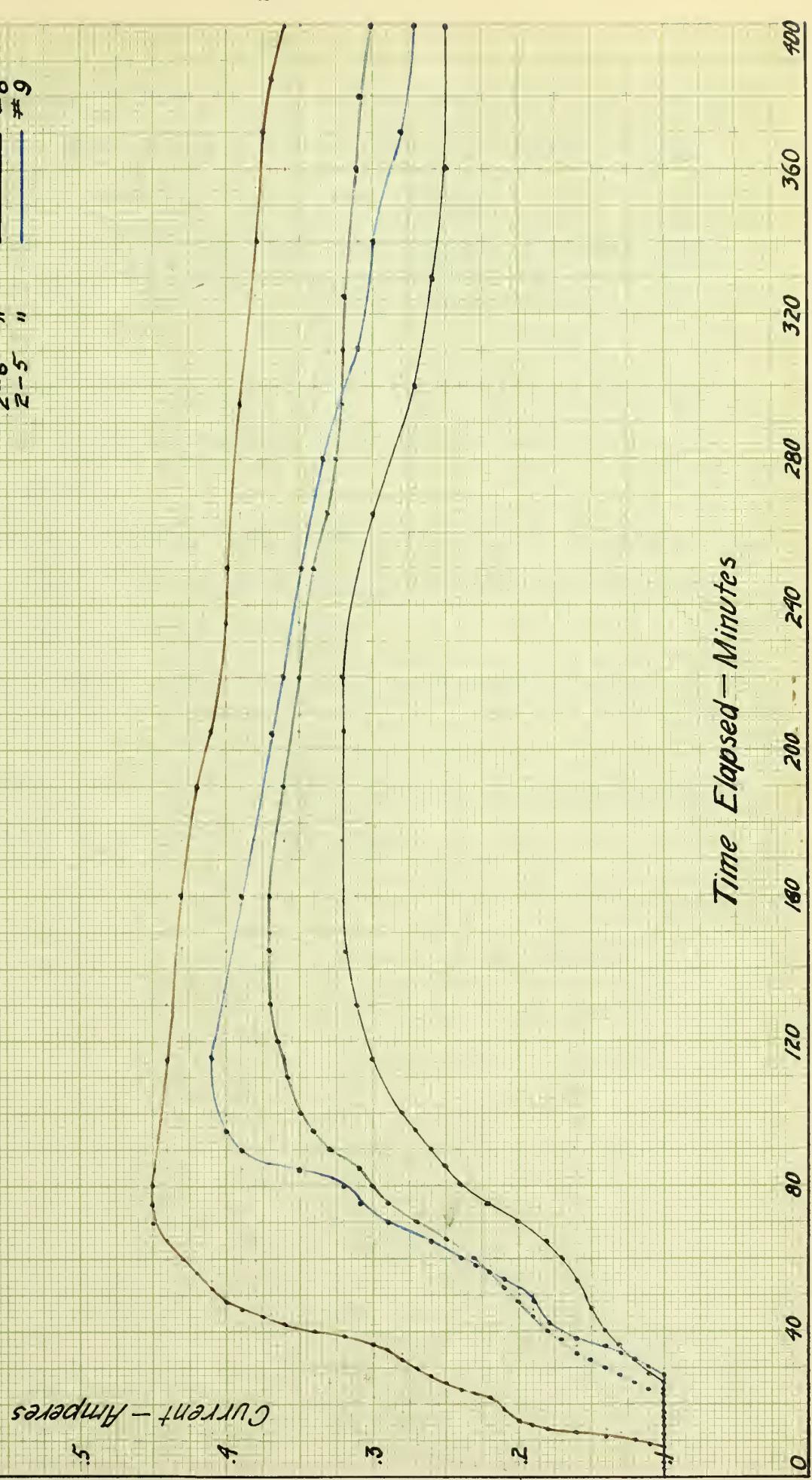


Figure II

From the curves it will be seen that there is a reduction in amperage down to the 6-6 minute anode when the results again show the tendency to a higher current.

Thus it may be concluded that for 30% Ni-steel, and double oxidation, that two 6 minutes of oxidation is the best.

For the single oxidation, that is for Exp. #10, 11, and 12, the results are given in Tab. III, page 19, and fig. III, page 21.

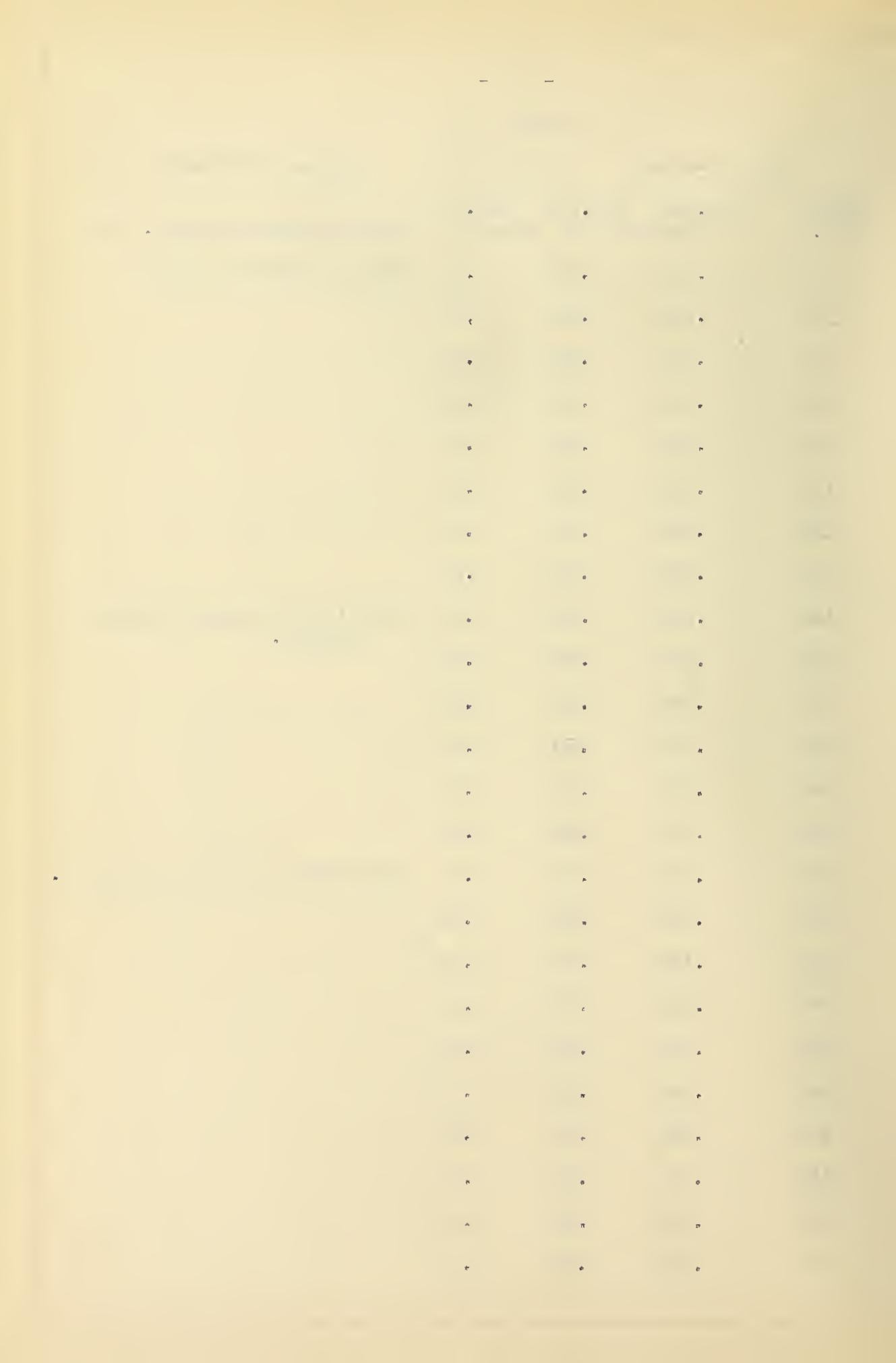
Here the amperage was double as compared to Exp. #6, 7, 8, and 9 for the same voltage, showing much less resistance in the oxide coating.

Again there is observed a minimum amperage when oxidized for one 15 minute period.

As Exp. #11 showed the best results, the observations noted in Tab. III are upon this anode.

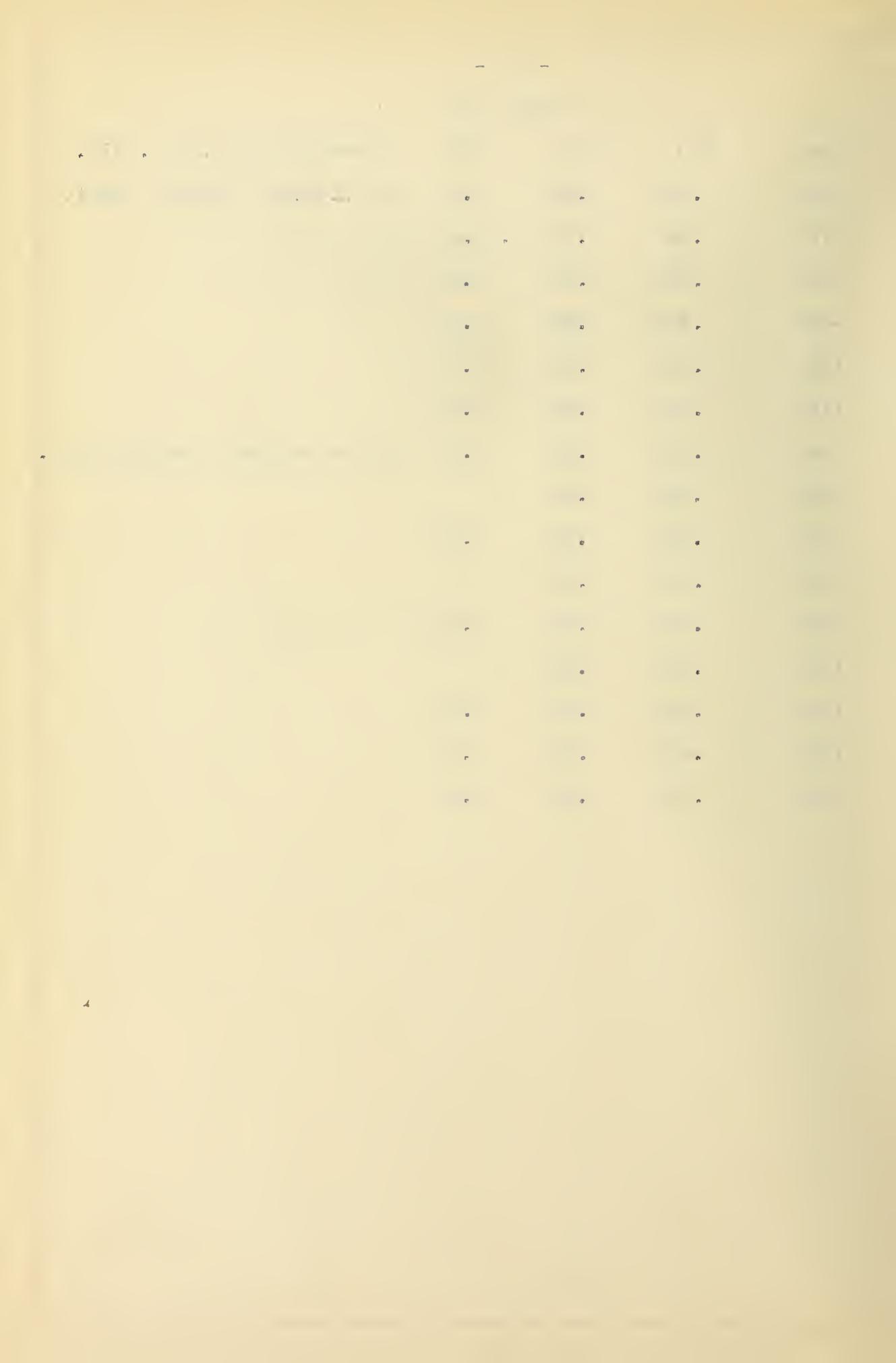
Tables III

Time min.	30% Ni-steel Exp. #10	Solution #1 Exp. #11 Current in amperes	Exp. #12	Constant Voltages 2 v. Observations on Exp. #11
0	.20	.20	.20	No evolution of gas.
2	.22	.22	,22	
4	.23	.24	.24	
6	.24	.26	.26	
8	.24	.26	.28	
10	.25	.27	.29	
12	.28	.27	.30	
14	.32	.28	.31	
16	.35	.28	.31	Flaking of anode surface begins.
18	.37	.28	.32	
20	.38	.29	.33	
22	.40	.30	.33	
24	.41	.32	.35	
26	.42	.33	.36	
28	.42	.34	.37	Cu begins to dep. on anode.
30	.43	.34	.38	
32	.43	.35	.38	
34	.43	.35	.39	
36	.44	.35	.40	
38	.44	.35	.40	
40	.44	.36	.40	
45	.44	.37	.40	
50	.43	.38	.40	
55	.43	.38	.41	



Tables III

Time	#10	#11	#12	Observations on Exp. #11.
60	.43	.38	.41	Cu on anode becomes cryst.
70	.43	.39	.41	
80	.42	.39	.41	
90	.42	.39	.42	
100	.42	.39	.42	
110	.41	.38	.43	
120	.41	.38	.43	Cu on cathode becomes cryst.
130	.40	.38		
140	.39	.37	.43	
150	.39	.37		
160	.39	.36	.43	
170	.39	.36		
180	.40	.35	.42	
190	.40	.34	.42	
200	.40	.34	.42	



- 21 -

**Amperage-Time Curve
of 30% Nickel-Steel at 2 Volts
Oxidized Various Periods.**

#10 #11 #12
 18 min 15 " 12 "

CURRENT - Amperes

.6

.5

.4

.3

.2

.1

0

Time Elapsed - minutes

80

90

100

110

120

130

140

150

160

170

180

190

200

Figure III

Part IV

Conclusions

As will be seen the results were not successful as to producing a new anode. However they are conclusive in the study of the oxide, effect of time and method of oxidation, and effect of voltage and current density. Thus these results may be used in the further study of the anode especially in terms of oxide coatings.

It was observed that the higher Ni-steel alloy showed less corrosion and a greater adaptability to take on a protective coating of oxide as shown by lower amperage and corrosion of anode.

That double oxidation gives better coatings than single oxidation as shown between the amperages in Tab. II and III.

That a minimum amperage may be obtained for a given alloy by oxidizing for a certain length of time, either for double oxidation or single oxidation as shown by curves on fig. II and III.

Part V

Suggestions

Better results may be obtained by hammering the anode as it is withdrawn at the red heat from the niter bath, then after sufficient treatment in this way it should be given a final bath without hammering. The theory is to get the oxide coating as dense as possible.

Another attempt would be the fusion of the oxide coating if possible by heating to the fusion point of the oxide. This would tend to approach the quality of fused magnetite mixed with nickolous oxide.

Also similar tests should be run on ferro-chrome and ferro-silicon alloys with oxide coating.

The study of aluminium alloys seems plausible due to the low position of aluminium in the electromotive scale.

Also, if available, experiment should be made on a new alloy developed in Italy, known as biakmetal. The approximate composition is this

Metal	Range	Average
Copper	35-44%	40%
Iron	1.5-4.75	3
Tungsten	3-6	3
Nickel	60.5-45.25	54

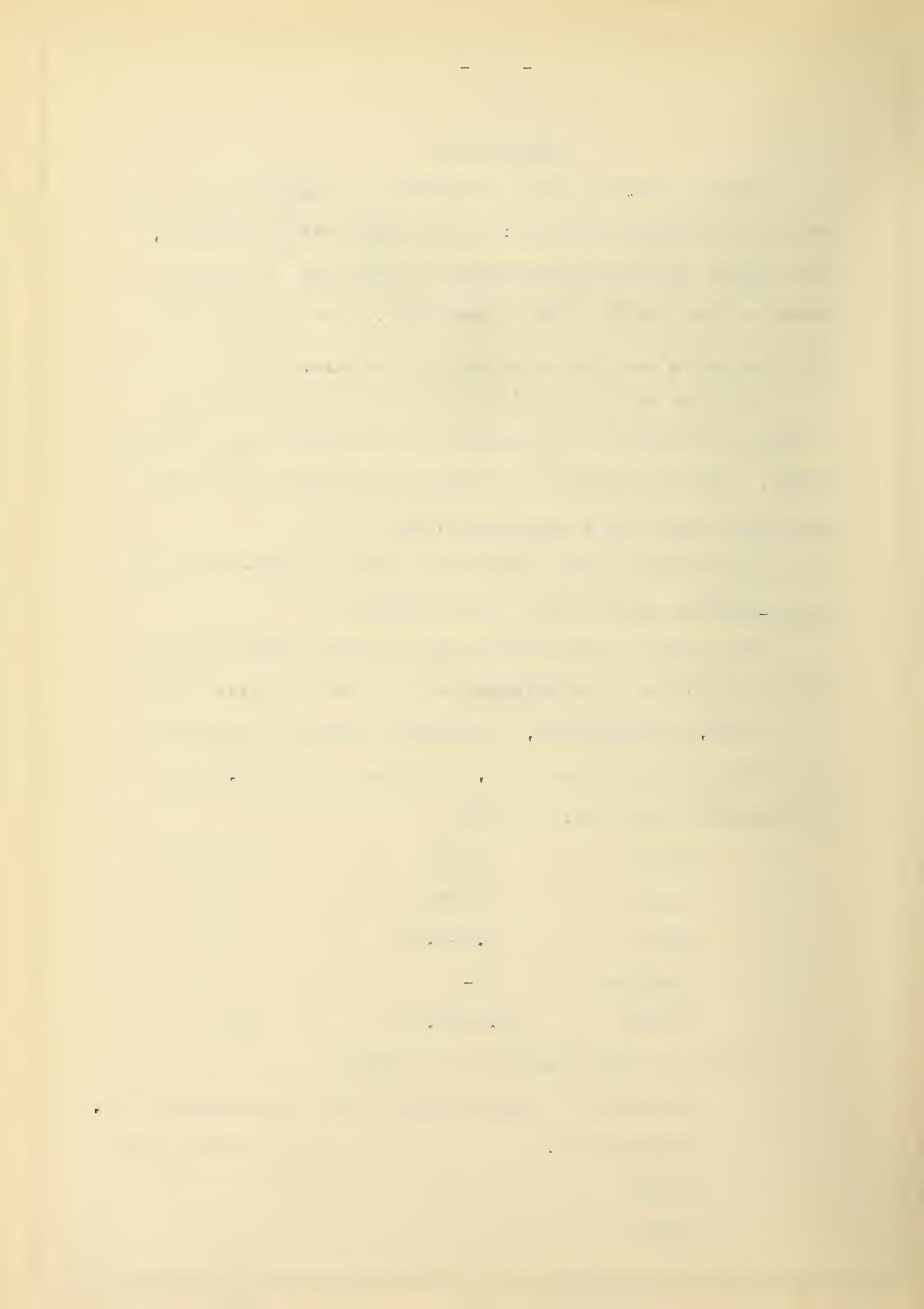
Acid resisting qualities are these:

Sulphuric any strength under 100 degrees Cent.

Hydrochloric " " " any temperature.

Acetic " " " "

Citric " " " "



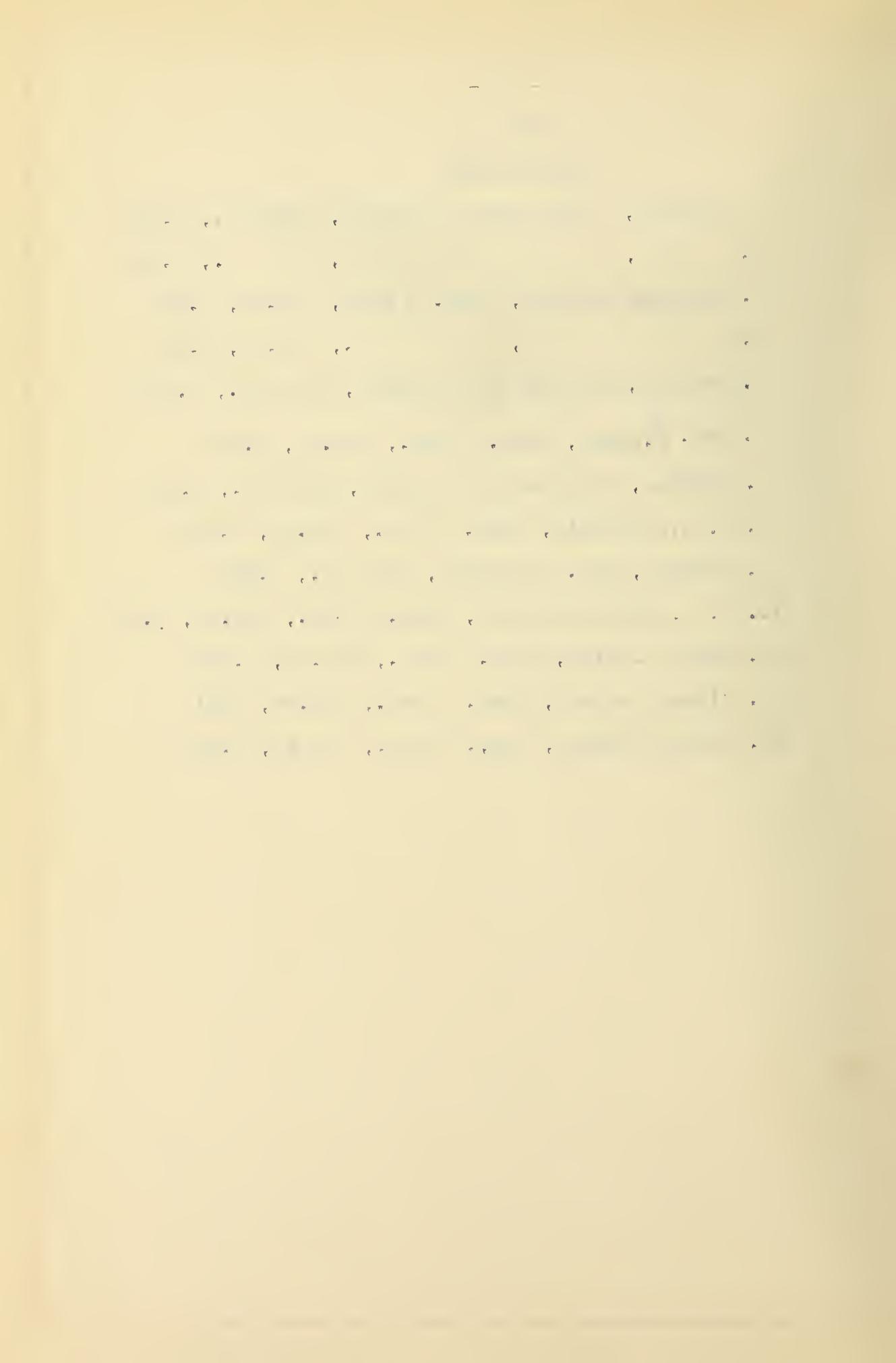
Tannic any strength, any temperature

Cold nitric up to 1.40 SP. gr.

Part VI

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